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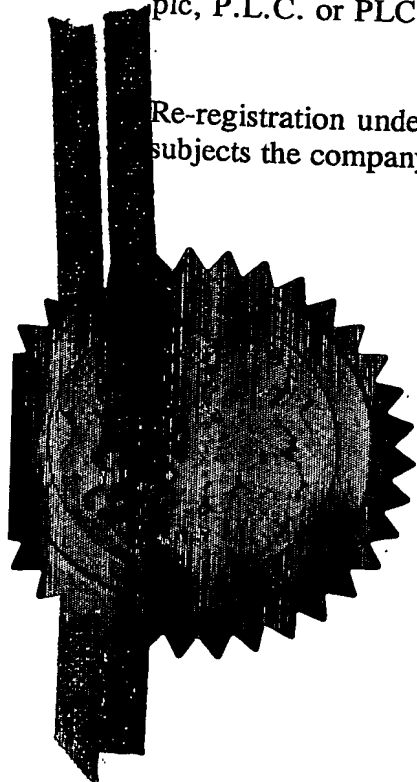
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1. Your reference

PAI 51121/CB

2. Patent application number

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19 DEC 2003

0329415.4

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Imperial Chemical Industries Plc
20 Manchester Square
London, W1U 3AN

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

735006

4. Title of the invention

A MODIFIED BINDER POLYMER FOR COATING COMPOSITIONS

5. Name of your agent (if you have one)

ANDREW FRANKOU

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

ICI Paints
ICI Group Intellectual Property
P O Box 1883
Wexham Road
Slough PDO
Berkshire SL2 5FD

Patents ADP number (if you know it)

6366090003

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

GB

0312916.0

5 June 2003

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

N/A

Date of filing
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

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Description

41

Claim(s)

3

Abstract

1

Drawing(s)

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Statement of inventorship and right to grant of a patent (Patents Form 7/77)

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11.

Andrew Frangou

I/We request the grant of a patent on the basis of this application.

Signature

ANDREW FRANGOU

Date 19th Dec 2003
(Agent for Applicant) (19/12/03)

12. Name and daytime telephone number of person to contact in the United Kingdom

ANDREW FRANGOU

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A MODIFIED BINDER POLYMER FOR COATING COMPOSITIONS

This invention relates to a modified film-forming binder polymer for a coating composition and to coating compositions containing the modified polymer. The modified polymer is especially useful in architectural coating compositions such as paints, varnishes or woodstains which can be applied
5 by brush, roller or pad at ambient temperatures of say 0 to 30°C to surfaces associated with buildings, furniture or fittings found in or around buildings. For brevity, all such architectural coating compositions will be referred to as "paints".

All aqueous architectural paints contain film-forming binder polymer.
10 As a coating of liquid paint dries on a surface, this film-forming binder polymer serves to form a film (i.e. a dried coat) of paint which bonds to the surface and also binds together all the non-volatile components of the paint including particularly any opacifiers, pigments and extenders present.

A wide variety of conventional film-forming binder polymers are available, but those most commonly used in aqueous architectural paints are of three broad types obtained from mono-ethylenically unsaturated monomers and known colloquially as the "acrylics", the "vinyls" and the "styrenics". The "acrylics" are usually copolymers of at least two alkyl esters of one or more mono-ethylenically unsaturated carboxylic acids (e.g. methyl methacrylate-butyl acrylate copolymer) whilst the "vinyls" usually comprise copolymers of a mono-vinyl ester of a saturated carboxylic acid and at least one of either an acrylic monomer or a different mono-vinyl ester. The "styrenics" are copolymers containing styrene (or a similar mono-vinyl aromatic monomer) together with a copolymerisable monomer which is usually an acrylic.

Such film-forming binder polymers may be produced as solution copolymers or dispersion copolymers in a carrier liquid. Solution copolymers are substantially dissolved in the carrier liquid whereas dispersion copolymers are produced as discrete particles in the carrier liquid. The solventborne or aqueous dispersions of particles require stabilisers, sometime referred to as emulsifiers or surfactants, to prevent the particles from flocculating and forming a sediment, thereby improving the storage and shear stability of the dispersion. The carrier liquid may be organic solvent or an aqueous medium. Typically the carrier liquid used to

make a solution copolymer is a liquid which is a good solvent for the copolymer concerned such that the copolymer is substantially dissolved in it. Where the carrier liquid is aqueous, at least 50% by weight of the liquid is water with the remainder being water compatible organic solvent or solvent mixture.

Such solution or dispersion copolymers useful as film forming binder polymers, whether solventborne or waterborne can be made by well-known solution polymerisation or emulsion polymerisation methods respectively.

Paints containing aqueous dispersions of particles of conventional film-forming binder polymers apply well to surfaces at warmer temperatures of say above 10°C but if they are applied at low temperatures, the dried coats of paint formed are prone to cracking and consequently poor scrub resistance. Cracking occurs because the low temperatures impede the coalescence of the binder polymer particles into a film. Coalescence can be improved by adding organic so-called "coalescing solvents" to the paint formulation and typical of such organic solvents are ethylene glycol, propylene glycol, benzyl alcohol and the proprietary solvent called "Texanol" which is trimethylpentane diol isobutyrate. Nowadays such solvents are considered to be environmentally unfriendly and so an alternative solution to the cracking problem has been to use binder polymers having much lower glass transition temperatures (T_g) despite the known

disadvantages of such low Tgs. The first disadvantage is a reduction in scrub-resistance. The second disadvantage is that the tackiness associated with newly applied dried coats of paint persists for longer. Glass transition temperature, Tg, is defined in European Patent Specification EP 0 425 085A, the contents of which are herein incorporated by reference.

Opaque paints often contain particulate pigments such as titanium dioxide in the form of rutile as an opacifying white pigment. The rutile particles are coated with other oxides to minimise any tendency for rutile to promote light induced degradation and so the rutile is expensive. Rutile also detracts from the scrub-resistance of a dried coat of paint if used in a high concentration in the paint formulation.

The amount of pigment in a dry paint film is an important feature as it can affect, for example, the final colour, opacity, hardness and scratch resistance of the dried paint. It is usually expressed as the volume of the pigment contained in the dry film compared with the total volume of the dried paint (including binder). This ratio is generally referred to as the Pigment Volume Concentration or PVC of the paint and expressed as a percentage. Other non-film forming particulate materials such as fillers and extenders, for example China Clay, may be included in the calculation to give the total PVC, expressed here as PVC(total) to distinguish it from

PVC(TiO_2) which refers to the PVC resulting only from the titanium dioxide content of the paint.

Opacifying pigments such as titanium dioxide can be expensive as well as having detrimental effects on paint properties such as scrub resistance and durability. Any improvement in opacity of the paint can be exploited by reducing the cost of the paint or improving the opacity so that fewer coats of paints are required. This is particularly important in pastel shades and whites as such colours are usually of low opacity.

It is an object of this invention to provide a modified film-forming binder polymer for a coating composition which at least minimises and usually avoids the need for the coating composition to contain an organic coalescing solvent without inducing film cracking or creating poor scrub-resistance and persistent tackiness in a dried coat of paint. An alternative object is to improve the opacity of coating compositions. A further alternative object is to promote the opacifying and pigmenting efficiency of titanium dioxide, especially rutile so that less of it is needed in a formulation to achieve a given opacity. A still further object of the invention is to provide coating compositions containing the modified film-forming binder polymer.

Accordingly, this invention provides a film-forming binder polymer for a coating composition wherein the polymer is modified by the presence

of bonded moieties (preferably furanose moieties) obtainable from plant fibre gum. Preferably, corn fibre gum is used. More preferably, the corn fibre gum is used at a level of from 0.1wt % to 5wt%, even more preferably from 2wt% to 4wt%, based on the total binder polymer.

5 The term bonded is intended to include not only the situation where the plant fibre gum moieties and the film forming binder polymer are chemically combined by, for example covalent bonds, but also when they exist as an intimate mixture. Where the modified film forming binder polymer is a dispersion, it is preferred that the majority, preferably all of the
10 particles are each substantially comprised of both the binder polymer and the plant fibre gum moieties whether chemically combined or as a mixture. Even more preferably, the particles are of the core shell type.

Plant fibre gum is obtainable from the fibrous parts of various plants, typically originating from the husk or seed case. A ready source of plant
15 fibre is corn or maize from which the corn fibre gum is extractable using the process disclosed in United States Patent Specification US 6,147,206 published on 14 November 2000, the contents of which are herein incorporated by reference. Other suitable examples of plants from which plant fibre gum may be extracted include wheat and tapioca.

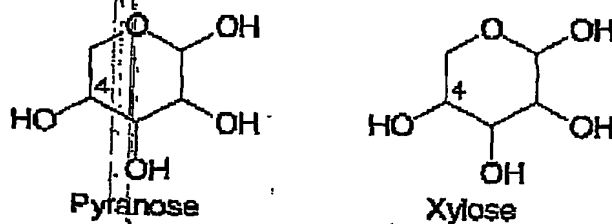
20 Corn fibre gum is a well known product described for example in the paper "Potential New Uses for Corn Fiber" given by K. B Hicks et al during

the Proceedings of the Corn Utilization & Technology Conference, Kansas City, USA held on 2 to 5 June 2002 and published by the National Corn Growers Association and Corn Refiners Association, see pages 122 to 127. The content of these pages is herein incorporated by reference. Hicks et al
5 report that corn fibre is a substantial by-product of corn milling from which corn fibre gum can be extracted and has been extracted for at least 50 years. A typical extraction comprises heating the corn fibre to 70°C in alkaline hydrogen peroxide to yield the gum which can be spray dried to give a free flowing powder which is easily re-dissolved in water. Details of a useful
10 extraction technique are given in United States Patent Specification US 6 147 206.

A typical corn fibre gum is a polysaccharide usually composed of about 35wt% of arabinose (which is an approximate equimolar mixture of furanose and pyranose) together with about 50wt% of xylose and about
15 10wt% of a mixture of glucuronic acid and galactose, the remainder consisting of a mixture of two or more of the following, glucose, mannose, ribose and rhamnose. Such materials are also sometimes referred to as arabinoxylans and glucuronoarabinoxylans.

Galactose and glucuronic acid are present in a weight ratio of about
20 2:1. Pyranose and xylose have the structural formulae, differing only at the carbon 4 position where pyranose has the hydroxyl group above the ring

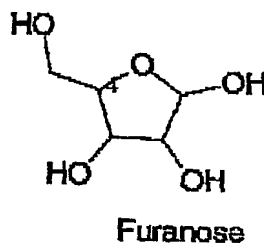
whereas in xylose the hydroxyl group is below the ring. Note that the protons on the ring carbons have been omitted for simplicity.



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Furanose has the structural formula shown below where there is a very labile hydrogen atom at carbon 4 which is thought to readily take part in chemical reactions including bonding to conventional monomers during

10



polymerisation processes in which they form binder polymers. The lability of the hydrogen at position 4 is described in an article by Gilbert et al. on pages 1565 to 1572 of the Perkin Transactions (Volume 2) of the Journal of the Chemical Society of 1998, the contents of which pages are herein incorporated by reference. It has been found that coating compositions containing the modified binder polymer require minimal and usually zero amounts of an organic coalescing solvent yet do not suffer from significant

15

film cracking, poor scrub resistance or excessively persistent tackiness in a dried coat of the composition. Also, the opacity of coating compositions is improved.

The examples of suitable mono-ethylenically unsaturated monomers
5 used to make conventional (that is unmodified) polymers are also suitable for making the binder polymers modified with corn fibre gum. Such monomers include:

- 10 a) "acrylics" such as alkyl (especially methyl, ethyl, ethylhexyl and n-butyl) esters of unsaturated carboxylic acids such as acrylic or methacrylic or fumaric acids or maleic anhydride,
- b) "vinyls" such as mono-vinyl esters (especially vinyl acetate or vinyl "Versatate"¹) and
- 15 c) "styrenics" which are usually styrene but which can be other monovinylidene aromatics such as vinyl toluene or vinyl pyridine and which are usually copolymerised with comonomers such as the ethyl or ethylhexyl or butyl acrylics mentioned above.

Various mono-ethylenically unsaturated acid or acid anhydride monomers may be copolymerised with the binder monomers to increase the hydrophilic character of the binder polymer in alkaline solutions. This is

¹ Vinyl "Versatate" is the vinyl ester of so-called "Versatic" acid which is a mixture of aliphatic monocarboxylic acids each containing an average of 9, 10 or 11 carbon atoms and is commercially available from the Shell Chemical Company of Carrington, England.

especially advantageous as it serves to increase the stability of the aqueous dispersions. However the acid comonomers usually do not exceed 7 mol % of the total monomers for otherwise the binder polymer becomes too hydrophilic to retain acceptable scrub-resistance.

5 Suitable acids include unsaturated carboxylic acids and in particular acrylic or methacrylic acids and unsaturated acid anhydrides include maleic anhydride. Acids or their anhydrides may allow some bonding of the binder polymer by ester formation to other hydroxylic moieties in the corn fibre gum in addition to the bonding to furanose by means of labile hydrogen.

10 It is desirable to choose combinations of monomers which include a sterically bulky monomer so as to result in binder polymers in which the chain moieties have a Tg of below 350K and preferably below 325K. Even more preferably the Tg is from 253K to 300K and most preferably from 263K to 283K. Preferred "acrylic" binder copolymers include copolymers
15 of methyl methacrylate with butyl acrylate or 2-ethylhexyl acrylate as sterically bulky monomers and optionally copolymerised with up to 7 mol % acrylic or methacrylic acid. Preferred "vinyl" binder copolymers include copolymers of vinyl acetate with a bulky monomer which is usually vinyl "Versatate" or bulky acrylic monomer as above plus the same optional acid
20 comonomers. Preferred "styrenic" binder copolymers include copolymers of styrene with butyl acrylate or 2-ethylhexyl acrylate serving as the bulky

monomers with optionally up to 7 mol % acid comonomers as above. T_g will be increased unacceptably by excessive crosslinking and so it is essential not to incorporate more than 7 wt % of a conjugated diene into the binder polymer and it is very much preferred to avoid any such diene.

5 Preferably the film forming binder polymer is carried in aqueous medium. This reduces the organic solvent lost to the atmosphere when a paint based on such a binder is used thereby minimising unpleasant odours, especially when painting in an enclosed space. More preferably it is an aqueous dispersion of polymer particles and most preferably it is made by
10 an emulsion polymerisation process.

If copolymerisation at superatmospheric pressures is commercially tolerable, the hydrophilic nature of the binder polymer can be adjusted downwards by including some mono-olefin (usually some ethylene) in the monomers. This will improve scrub-resistance.

15 The simplest way to produce a modified binder polymer is to add plant fibre gum, preferably corn fibre gum to the polymerisation reaction mixture from which the binder polymer is formed. More preferably the binder polymer has bonded moieties derived from furanose present in the reaction mixture from which the binder polymer is formed.

20 A process is also provided for modifying film forming binder polymers which are binder polymers for coating compositions wherein plant

fibre gum, preferably corn fibre gum, and/or furanose is added to the polymerisation reaction which produces the binder polymer. Such polymerisations are conventionally performed with the aid of free radical or redox initiators. The temperature at which the polymerisation is carried out depends on the boiling point of the carrier liquid used and the radical flux of the initiator selected. Where the modified binder polymer is made as a dispersion of polymer particles in water, the temperature is preferably from 20 to 98°C, more preferably from 30 to 95°C and most preferably from 50 to 90°C.

Without wishing to be bound by this, it is suspected that during the polymerisation the constituents of the plant fibre gum such as corn fibre gum are chemically incorporated into the copolymer, for example by abstraction of labile hydrogen from the furanose by the initiators. Preferably from 0.1 to 5wt% (and more preferably 2 to 4wt%) of plant fibre gum, more preferably corn fibre gum is added to the polymerisation reaction mixture where the percentages are based on the total weight of the monomers from which the binder polymer is to be formed.

A coating composition is also provided wherein the composition contains modified binder polymer as herein described. Preferably the coating composition further contains components usually found in paints such as pigments, fillers, extenders, rheological modifiers, dispersants,

antifoams, flow aids, crosslinkers and biocides. Preferably the coating composition contains pigment and more preferably the pigment is titanium dioxide. Even more preferably the pigment is rutile titanium dioxide. Preferably the PVC(TiO_2) is from 10 to 35%, more preferably from 12 to 5 30% and most preferably from 17 to 30%. The PVC(total) is preferably from 8 to 75% depending on the gloss or sheen level of the paint.

An aqueous dispersion of the modified film-forming binder copolymer is easily converted into a coating composition by mixing it with all the components of the composition except for, preferably any chelate 10 structuring agent. If a strongly structured composition, the chelate is preferably stirred in just before the composition is filled into cans so that the gel structure develops in the can.

The most significant of the other components are opacifying pigments such as rutile or anatase titanium dioxide or voided organic 15 polymer particles. Typical fillers and extenders include chalk, limestone, kaolin and talc. Silica may also be present as a matting agent. Whilst this invention is of most importance in making paints, it is also possible to omit the opacifier to produce a varnish or woodstain.

The coating compositions preferably have a "Rotothinner" (low 20 shear) viscosity of from 0.15 to 3.0 pascal.sec all measured at 25°C using a 5.6cm diameter spindle rotating at 560 rpm. A strongly structured

thixotropic composition preferably has a gel strength at 1 week of at least 50g.cm.

The coating composition is preferably solventborne or waterborne. Waterborne compositions are preferred whereby at least 50% by weight of the carrier liquid in the composition is water. Such compositions release less organic solvents into the atmosphere and are also preferred by users as they also have reduced odour.

The use of the modified binder polymer in a coating composition improves the opacity of the coating composition. It is not known by which mechanism this occurs, although and without wishing to be bound by this, it is thought that the opacifying efficiency of pigments such as titanium dioxide, especially rutile is increased by from 10 to 20%. This allows a greater opacity to be achieved or alternatively reduced concentrations of rutile with a consequent improvement in scrub-resistance and cost.

Accordingly, the invention also provides a method for improving the opacity of coating compositions by employing a modified binder polymer as a binder polymer in a coating composition. Preferably the coating composition contains particulate non-film forming material and more preferably it is titanium dioxide, especially in the form of rutile.

The invention will now be illustrated by the following Examples of which Examples A to E are comparative.

The paints were tested for opacity and scrub-resistance as follows:

ISO Opacity Test:

A clean transparent polypropylene sheet 280 mm long by 104 mm wide is mounted on a clean transparent glass plate using adhesive tape. The
5 sheet provides a surface to which a coat of paint under test can be applied.

The paint under test is passed through an 80 μm nylon mesh filter to remove any poorly dispersed particles and then it is de-aerated under vacuum. Any surface skin should be removed.

A coat of the de-aerated paint is applied to the polypropylene
10 surface using a 175 μm block spreader (1 μm equals 10^{-6} m) and the coat is allowed to dry at room temperature for 16 hours. Next, the dried coat is inspected for defects by placing the glass plate over a light box and any defective coats must be rejected.

The CIE X, Y, Z values of the dried coat are determined using a
15 spectrophotometer calibrated against a standard white and a standard black tile. The X, Y, Z values are then used to calculate the Kubelka-Munk Scatter Coefficient which is a good indication of opacity.

Alternatively, the contrast ratio can be measured according to the following procedure. The paint is spread over a Morest chart Number 9
20 using a K-bar 6 to give a wet paint film of approximately 60 μm . The paint is allowed to dry over a period of from 2 to 3 hours at a temperature of

about 20°C. One half of the Morest chart is coloured black and the other white. A Spectroflash 600 PLUS spectrophotometer is used to measure the reflected light from the dried paint applied over first the black and then the white half of the Morest chart. The amount of measured light reflected on the black half is divided by the amount reflected from the white side and expressed as a percentage contrast ratio. The measurements are repeated three times and averaged.

ISO Scrub Resistance Test:

A coat of paint is applied to each of four polypropylene panels as in the opacity test above except that a 400 µm block spreader is used. The coats are allowed to dry for 28 days at 23°C in a 50% humidity. Next the dried coated panels are weighed, subjected to 200 cycles of rubbing in accordance with the ISO Scrub Test, EN 13300 Part 5.4, ISO 11998 and weighed again. The average weight loss for the four panels was taken and, together with the area of the rubbed surface and the density of the coat, was used to calculate the loss of thickness of the coat. This calculated loss of thickness is an inverse indication of scrub-resistance.

The ISO Test gives scrub-resistances numerical ratings as follows:

<u>Loss of Thickness</u>	<u>No. of Cycles</u>	<u>Rating</u>
Below 5µm	200	1

17

5 to 20µm	200	2
20 to 70µm	200	3
Below 70µm	40	4
Above 70µm	40	5

5

British Scrub Resistance Test:

The British Scrub Resistance Test is performed according to British Standard 7719 of 1994 and a weight loss is reported instead of a calculated loss of thickness.

10 "Bentone" Ew: Bentonite clay supplied by Rheox Ltd of UK

Corn Fibre Gum is obtainable by the process disclosed in US 6,147,206. A typical composition of Corn Fibre Gum obtained by this process is 48.1% xylose, 39.4% arabinose, 8.4% galactose and 4.2% glucuronic acid, all by weight.

15 "Dispelair" CF 246: A surfactant supplied by Blackburn Chemicals Ltd of Blackburn, UK

"Disponil" A1580: A surfactant supplied by Henkel Performance Chemicals of Germany

20 "Blanose" 7M 31C: A cellulosic thickener supplied by Hercules Inc of USA

"Britomya" V: A calcium carbonate supplied by OMYA UK Ltd of Surrey, UK

25

"Dispex" N40: A surfactant supplied by Allied Colloids of UK.

"Empimin" OT75: A surfactant supplied by Albright & Wilson of UK

- "Fordacal" 30: A calcium carbonate extender supplied by Foramin Co. Ltd of UK.
- "Lubrizol" 2405: A surfactant supplied by Lubrizol UK LTD of UK
- 5 "Mergal" 711 K6: A biocide supplied by Troy Chemicals Europe BV of the Netherlands.
- "Microdol" H 200: Dolomite supplied by Omya of Cologne, Germany.
- 10 "Natrosol" 250MR: A cellulosic thickener supplied by Hercules Inc of USA
- "Perlankrol" ESD60: A surfactant supplied by Akzo Nobel Chemicals Ltd of the Netherlands
- 15 "Rocima" V189: A biocide available from Thor Plastics UK, New Road, Newhaven, UK
- "Rhodacal" A246L: A surfactant supplied by Rhodia SA of France
- "Ropaque" ULTRA: A voided organic particulate opacifier supplied by Rohm & Haas of USA
- 20 "Tilcom" AT35: A chelate structuring agent supplied by Tioxide Specialists Ltd (Huntsman) of Teeside, UK

EXAMPLE 1

Production of a Modified Acrylic Binder Polymer:

Four preliminary charges were made up which will be referred to as the corn fibre gum charge, the seed monomer charge, the initiator charge (which was subsequently divided into three sub-charges) and the acrylic monomer charge. The corn fibre gum charge was made up by mixing together the following components:

<u>Component</u>	<u>Weight g</u>
Water	549.77
Corn Fibre gum	12.60
Sodium bicarbonate	1.20
Sodium chloride (pure and vacuum dried)	1.02
Surfactant Rhodacal A246L	<u>1.44</u>
Total Corn Fibre gum charge	566.03

The seed monomer charge was made up by mixing together the following components:

<u>Component</u>	<u>Weight g</u>
Vinyl Acetate	20.77
Vinyl "Versatate"	3.67
Surfactant "Empimin" OT75	<u>0.25</u>
Total Seed Monomer Charge	24.69

The initiator charge was made up by mixing together the following components:

<u>Component</u>	<u>Weight g</u>
Water	34.00
Ammonium persulphate	<u>1.60</u>
Total initiator charge	35.60

The initiator charge was then divided into three sub-charges. 45wt% of the charge became the seed initiator charge to which was then added 0.49g of the surfactant "Lubrizol" 2405. Another 45wt% of the charge became the main initiator charge and the remaining 10wt% became the "mop-up" initiator charge.

The acrylic monomer charge was made up by mixing together the following components one after another in the order shown in the list below:

<u>Component</u>	<u>Weight g</u>
Methyl methacrylate	229.10
Surfactant "Disponil" A1580	18.85
Surfactant "Perlankrol" ESD60	2.86
2-ethylhexyl acrylate	<u>219.62</u>
Total Acrylic Monomer Charge	470.43

In performing the polymerisation, the corn fibre gum charge was first purged with nitrogen for 5 minutes and then heated to 75°C and then held at that temperature for 30 minutes. The seed monomer charge was then added to the hot corn fibre gum charge and the whole was maintained at 75°C for a

further 10 minutes. The seed initiator sub-charge was then added and the temperature of the combined charges was increased to 90°C over 30 minutes during which time an aqueous dispersion of vinyl acetate/vinyl "Versatate" seed copolymer formed with possibly some bonding of moieties from the
5 corn fibre gum.

The acrylic monomer charge together with the main initiator sub-charge were added dropwise over a period of two hours to the dispersion of seed copolymer whilst the temperature was maintained at 90°C. During this time, an aqueous dispersion of seeded copolymer of methyl methacrylate
10 and 2-ethylhexyl acrylate formed with bonding of moieties from the corn fibre gum. On completion of the addition of the acrylic monomers, the "mop-up" initiator sub-charge was added and the temperature maintained at 90°C for a final 30 minutes after which the dispersion was allowed to cool to 37°C. The dispersion consisted of particles of seeded acrylic copolymer
15 containing 2.5wt% of bonded corn fibre moieties which had bonded either during the seed copolymerisation or during the main polymerisation and quite probably during both. In the copolymer, 5wt% was vinyl seed and the ratio of copolymerised methyl methacrylate to 2-ethylhexyl acrylate was 1:1.

20 A solution of 1.5g an isothiazoline based biocide in 4g water was added to the cooled dispersion.

EXAMPLE 2

Production of a Modified Vinyl Binder Polymer:

Five preliminary charges were made up which will be referred to as the corn fibre gum charge, the initiator charge (which was subsequently divided into three sub-charges), the vinyl monomer charge, the oxidant charge and the reductant charge. The corn fibre gum charge was made up by mixing together the following components:

<u>Component</u>	<u>Weight g</u>
Water	423.96
Corn Fibre gum	12.62
Sodium bicarbonate	1.20
Surfactant Rhodacal A246L	<u>1.44</u>
Total Corn Fibre gum charge	439.22

The initiator charge was made up by mixing together the following components:

<u>Component</u>	<u>Weight g</u>
Water	39.66
Ammonium persulphate	1.70
Surfactant "Lubrizol" 2405	<u>2.17</u>
Total initiator charge	43.53

The initiator charge was then divided into three sub-charges. 30wt% of the charge became a seed initiator charge. Another 50wt% of the charge became the main initiator charge and the remaining 20wt% became a "mop-up" initiator charge.

The vinyl monomer charge was made up by mixing together the following components one after another in the order shown in the list below:

	<u>Component</u>	<u>Weight g</u>
5	Vinyl Acetate	415.96
	Surfactant "Empimin" OT75	5.06
	Vinyl "Versatate"	<u>73.40</u>
	Total Vinyl Monomer Charge	494.42

The oxidant charge was made up by mixing together the following components:

	<u>Component</u>	<u>Weight g</u>
	Water	4.71
	Tertiary butyl hydroperoxide	<u>1.00</u>
	Total Oxidant Charge	5.71

The reductant charge was made up by mixing together the following components:

	<u>Component</u>	<u>Weight g</u>
	Water	6.81
20	Sodium metabisulphite	<u>1.00</u>
	Total Reductant Charge	6.81

In performing the polymerisation, the corn fibre gum charge was first purged with nitrogen for 5 minutes and then heated to 65°C and maintained at that temperature for 30 minutes. 2.5wt % of the vinyl monomer

charge was then added to the hot corn fibre gum charge as a seed quantity and the whole was maintained at 65°C for 10 minutes. The seed initiator sub-charge was then added and the temperature of the combined charges was raised to 85°C for 30 minutes during which time an aqueous dispersion of vinyl acetate/vinyl "Versatate" seed copolymer formed with possibly some bonding of moieties from the corn fibre gum.

The remaining vinyl monomer charge together with the main initiator sub-charge were added dropwise over a period of three hours to the dispersion of seed copolymer whilst the temperature was maintained at 85°C. During this time, an aqueous dispersion of seeded copolymer of vinyl acetate and vinyl "Versatate" formed with bonding of moieties from the corn fibre gum. On completion of the addition of the vinyl monomers, the "mop-up" initiator sub-charge was added and the temperature maintained at 85°C for a final 30 minutes. Next the oxidant charge was added and the temperature maintained at 70°C for 5 minutes and then the temperature was reduced to 60°C and the reductant charge was added and the temperature was maintained at 60°C for a further 5 minutes. The dispersion was allowed to cool to 37°C and was found to consist of particles of seeded vinyl copolymer to which corn fibre moieties had bonded either during the seed copolymerisation or during the main polymerisation and quite probably during both.

A solution of 1.7g an isothiazaoline based biocide in 6.61g water was added to the cooled dispersion.

EXAMPLE 3
AND
COMPARATIVE EXAMPLE A

Preparation and Testing of Acrylic Silk Paint:

An acrylic silk paint (i.e. paint having a low pigment volume concentration or "PVC" of 20.5%) was prepared using either the aqueous dispersion of modified acrylic binder copolymer made in Example 1 (Example 3) or an aqueous dispersion made according to Comparative Resin Example D except that the monomer composition was 281.05g of methyl methacrylate, 5.34g of methacrylic acid and 313.12 g of 2-ethyl hexyl acrylate (Comparative Example A), together with the ingredients as listed in Table 1. The paint was then tested for opacity and ISO scrub-resistance and the results are given in Table 2.

In Example 3, a millbase of water, extenders, rutile and various other additives was made using a "Dispermat" rotatable blade mixer in which the blade was rotated at 300 rpm for low speed mixing and at 3 000 rpm for high speed mixing. To begin, the ingredients for Example 3 in Batch A in Table 1

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TABLE 1
INGREDIENTS FOR ACRYLIC SILK PAINTS

Example	3	A
Ingredient and Amount Used	g	g
BATCH A		
Water	135	172
"Bentone" EW bentonite clay	2.9	2.9
"Displex" N4D surfactant	1.9	1.9
"Dispelair" CF 246 antifoaming agent	1.0	1.0
"Mergal" 711K6 biocide	1.5	1.5
BATCH B		
"Britomya" V calcium carbonate	54.5	54.5
Rutile TR92	144	164
BATCH C		
Water	31	31
"Blanose" 7M31C cellulosic thickener	4.5	6.4
Water	73.3	73.3
"Dispelair" CF246 antifoaming agent	1.0	1.0
Water	10.0	10.0
BATCH D		
*Aqueous dispersion of binder copolymer	503	450
Ammonia	0.2	0.2
"Dispelair" CF246 antifoaming agent	1.0	1.0
"Tilecom" AT35 structuring agent	2.0	2.0
Water	—	30

* The concentrations of the copolymer in the dispersion were adjusted to ensure that both paints had a PVC of 20%. were added to the mixer at subjected to low speed mixing for 10 minutes. Next, the ingredients of Batch B were added to the contents of the mixer and all were subjected to high speed mixing for 20 minutes. Next, the first quantity of water and the "Blanose" of Batch C were added to the contents of the mixer and all were subjected to high speed mixing for 10 minutes. Then the second quantity of water and the "Dispelair" of Batch C were added to the contents of the mixer and all were subjected to high speed mixing for 10 minutes. Finally the millbase was completed by adding the last quantity of watch from Batch C and subjecting the contents of the mixer to low speed mixing.

The silk paint was made by adding the ingredients of Batch D in turn to the millbase in the mixer whilst maintaining low speed mixing. First the aqueous dispersion of acrylic binder copolymer was added slowly over a period of five minutes. Then the other ingredients were added one after another to complete the paint. The paint was allowed to stand for 16 hours at room temperature to enable the "Tilcom" to create structure and then the paint was ready for subjecting to the opacity and ISO scrub resistance tests the results obtained are shown in Table 2.

TABLE 2

OPACITY AND SCRUB-RESISTANCE TEST RESULTS (ACRYLIC SILK PAINTS)

Example	Rutile Content g	"Blanose" Content g	Kubelka- Munk Scatter Coefficient	ISO Scrub Resistance	
				Thickness Lost μm	ISO Rating
3	144	4.5	8986	1.0	1
A	164	6.4	9061	2.9	1

5 The PVC(total) of Example 3 was 19.9% and the PVC(TiO_2) was 12.7%.
The PVC(total) of Comparative Example a was 20.1% and the PVC(TiO_2)
was 13.4%.

EXAMPLE 4 AND COMPARATIVE EXAMPLE B

Preparation and Testing of Acrylic Matt Paint:

15 An acrylic matt paint i.e. of high PVC(total) was prepared using a
procedure similar to that employed for Example 3 but using ingredients as
specified in Table 3. As in Example 3 relating to silk paint, Example 4
employed the aqueous dispersion of acrylic binder copolymer made in
Example 1 whilst Comparative Example B employed the corresponding
Comparative Resin Example D except that the monomer composition was
20 281.05g of methyl methacrylate, 5.34g of methacrylic acid and 313.12 g of

2-ethyl hexyl acrylate (Comparative Example B), together with the ingredients as listed in Table 3.

TABLE 3

INGREDIENTS FOR ACRYLIC MATT PAINTS

Ingredient and Amount Used	Example 4 g	B g
BATCH A		
Water	150	150
"Displex" N40 surfactant	3.1	3.1
"Dispelair" CF246 antifoam agent	1.0	1.0
"Meral" 711 K6 biocide	1.5	1.5
BATCH B		
"Britomya" V calcium carbonate	55	55
"Fordacal" 30	123	123
China clay supreme	57	57
Rutile TR92	126	143
BATCH C		
Water	130	130
"Natrosol" cellulosic thickener	5.0	6.7
Water	42.8	42.8
"Dispelair" CF 246	1.0	1.0
BATCH D		
Aqueous dispersion of binder copolymer	207	173
"Ropaque" voided particle opacifier	8.1	8.1
"Dispelair" CF 246	1.0	1.0
"Tilcom" AT35 structuring agent	4.0	4.0
Water	--	26

In Example 4, a millbase was made by adding the ingredients of Batch A, Table 3 to a "Dispermat" mixer. The contents of the mixer were subjected to 10 minutes of low speed (300 rpm) mixing and then the

ingredients from Batch B were added slowly and the whole subjected to high speed (3 000 rpm) mixing for 20 minutes. Next the first quantity of water and the "Natrosol" from Batch C were slowly added to the contents of the mixer and the whole were subjected to 10 minutes of high speed mixing. Finally the millbase was completed by adding the last quantity of water and the "Dispelair" from Batch whilst subjecting all the contents to slow speed mixing.

The matt paint was made by adding the ingredients of Batch D in turn to the millbase in the mixer whilst maintaining the slow speed mixing. First the aqueous dispersion of the acrylic binder copolymer was added slowly over a period of five minutes. Then the other ingredients from Batch D were added one after another to complete the paint. The paint was allowed to stand for 16 hours at room temperature to enable the "Tilcom" to create some structure and then paint was ready for subjecting to the opacity and ISO scrub-resistance tests.

In Comparative Example B the procedure was repeated but using the corresponding unmodified acrylic copolymer. The paints were subjected to the opacity and ISO scrub-resistance tests and the results are shown in Table 4.

TABLE 4

OPACITY AND SCRUB-RESISTANCE
TEST RESULTS (ACRYLIC MATT PAINTS)

Example	Rutile Content g	"Natrosol" Content g	Kubelka- Monk Scatter Coefficient	Scrub Resistance	
				Thickness Lost μm	ISO Rating
4	126	5.0	10633	15.2	2
B	143	6.7	10431	17.8	2

The PVC(total) of Example 4 was 62.7% and the PVC(TiO_2) was 12.4%.

The PVC(total) of Comparative Example B was 63.0% and the PVC(TiO_2) was 13.8%.

EXAMPLE 5
AND
COMPARATIVE EXAMPLE C

Preparation and Testing of Vinyl Matt Paint:

A vinyl matt paint of PVC(total) 45% was prepared using a procedure similar to that employed for Example 4 but using the dispersion of modified vinyl binder copolymer made in Example 2 and the ingredients as specified

in Table 5 whilst Comparative Example C employed the corresponding unmodified vinyl binder polymer.

TABLE 5
INGREDIENTS FOR VINYL MATT PAINTS

Example	5	C
Ingredient and Amount Used	g	g
BATCH A		
Water	150	150
"Bentone" BW bentonite clay	2.0	2.0
"Displex" N40 surfactant	2.0	2.0
"Dispelair" CF246 antifoam agent	0.5	0.5
"Meral" 711 K6 biocide	0.5	0.5
"Disponil" A1580: A surfactant	5.0	5.0
BATCH B		
"Micropdol" H 200 dolomite	39	39
"Fordacal" 30	74	74
China clay	49	49
Rutile TR92	133	133
BATCH C		
Water	150	150
"Blanose" cellulosic thickener	5.0	6.5
Water	120	120
BATCH D		
"Dispelair" CF 246	0.5	0.5
Biocide	0.2	0.2
Water	10	10
Aqueous dispersion of vinyl binder copolymer	300	300

Ammonia to pH 8.5	0.04	0.04
"Ropaque" voided particle opacifier	48	48
"Dispelair" CF 246	1.6	1.6

In Example 5, a millbase was made by adding the ingredients of Batch A, Table 3 in turn to a "Dispermat" mixer. The contents of the mixer were subjected to 10 minutes of low speed (300 rpm) mixing and then the ingredients from Batch B were added slowly in turn and the whole subjected to high speed (3 000 rpm) mixing for 20 minutes. Next the first quantity of water and the "Blanose" from Batch C were slowly added to the contents of the mixer and the whole were subjected to 10 minutes of high speed mixing. Finally the millbase was completed by adding the last quantity of water from Batch C whilst subjecting all the contents to slow speed mixing.

The matt vinyl paint was made by adding the first amount of "Dispelair", biocide and water of Batch D in turn to the millbase in the mixer whilst maintaining the slow speed mixing. Next the aqueous dispersion of the vinyl binder copolymer was added slowly with the ammonia (to achieve a pH of 8.5) over a period of five minutes. Then the "Ropaque" and second amount of "Dispelair" from Batch D were added one after another with slow mixing to complete the paint. The paint was

subjected to the British scrub-resistance test and coats of the paints 400 μ m thick which had dried at below 8°C were examined visually for cracking.

In Comparative Example C the procedure was repeated but using the corresponding unmodified vinyl binder copolymer. The results the British scrub-resistance test and the visual examination are shown in Table 6.

TABLE 6

Example	Weight lost in British Scrub Test mg/cm ²	Observation of Cracking
S	1.64	Major Cracking
C	1.47	No Cracking

Tables 2, 4 and 6 show that the scrub-resistances of the paints containing modified and unmodified binder copolymers were, within experimental error, about equal. Tables 2 and 4 show that the opacifying efficiency of the rutile was improved by the use of the corn fibre gum modified binder polymer. Table 6 shows that the use of the corn fibre gum modified binder polymer overcomes the need to use coalescing solvents to prevent the cracking of coats of paint applied at low temperatures.

It was also observed that the tackiness of the dried coats of the paints according to Examples 3, 4 and 5 was lost at about the same rate as for commercial paints containing coalescing solvents.

Further modified acrylic binder polymers were made and converted to paint

Example 6

PRODUCTION OF A MODIFIED ACRYLIC BINDER POLYMER:-

A binder polymer similar to Example 1 was made using the components specified below and according to the process described in Example 1.

10. Corn Fibre Gum Charge

<u>Component</u>	<u>Weight g</u>
Water	578.35
Corn Fibre gum	13.86
Sodium bicarbonate	1.32
5. Sodium Chloride (pure and vacuum dried)	1.12
Surfactant Rhodacal A246 L	<u>1.58</u>
	592.63

Seed Monomer Charge

<u>Component</u>	<u>Weight g</u>
29 Vinyl acetate	22.85
Vinyl "Versatate"	4.04
Surfactant "Empimin"	<u>0.28</u>
	27.17

Seed Initiator Charge

<u>Component</u>	<u>Weight g</u>
------------------	-----------------

Ammonium persulphate	0.78
Water	17.07
Lubrizol 2405	<u>0.54</u>
	18.39

Acrylic Monomer Charge

<u>Component</u>	<u>Weight g</u>
Methyl methacrylate	229.10
Surfactant "Disponil" A 1580	18.85
Surfactant "Perlankrol" ESD60	2.86
2-Ethyl hexyl acrylic	<u>219.62</u>
	470.43

Main Initiator Charge for acrylic monomer feed

<u>Component</u>	<u>Weight g</u>
Ammonium persulphate	0.76
Water	<u>16.76</u>
	17.52

Mop-up initiator charge

<u>Component</u>	<u>Weight g</u>
Ammonium persulphate	0.18
Water	<u>3.90</u>
	4.08

Biocide solution

<u>Component</u>	<u>Weight g</u>
Rocima V189	1.65

Water

4.40
6.05A

Comparative Resin Example D

5 The following corn fibre gum free acrylic binder polymer was made.

Aqueous Charge

<u>Component</u>	<u>Weight g</u>
Water	499.93
Blanose 7L2C	3.32
Disponil A1580	2.58
Sodium bicarbonate	10.08
Sodium Chloride (pure and vacuum dried)	1.22
	517.13

15 The components of the aqueous charge were added to a round bottom reactor whilst stirring. The temperature of the contents was raised to 75°C.

During this heating period a monomer feed mixture was prepared in a separate vessel.

20 Monomer feed mixture

<u>Components</u>	<u>Weight g</u>
Methyl methacrylate	302.74
Acrylic acid (glacial)	6.00
Disponil A1580	23.81
ESD60	3.61
2-ethyl hexyl acrylate	290.76
	626.92

An amount of 31.35g of this mixture was removed from the vessel and added to the reactor. The temperature of the reactor contents was held at 75°C for a further 10 minutes during which time an initiator solution consisting of 1.87g of ammonium persulphate in 41.16g of water was made. 9.73g of the initiator solution were removed and added to the reactor. After 10 minutes the seed polymer formed and the temperature was raised over 30 minutes to 90°C. The remaining monomer feed mixture of 595.57g was added to the reactor over two hours during which time 28.01g of the initiator solution were also added. At the end of this period the remaining initiator solution of 5.29g was added to the reactor and held at 90°C for a further hour to ensure complete polymerisation of the monomers.

EXAMPLE 7 AND COMPARATIVE EXAMPLE E

Preparation and Testing of Acrylic Matt Paints

Example 7

A mill base was prepared as follows. An initial charge of 187.8g of water was added to a 1 litre disperser container followed by 20.2g of Orotan 731 and 1.5g Dispelair CF246. The mixture was stirred for 5-6 minutes at about 1000rpm using a high speed disperser fitted with a 7cm Cowles blade. 121.2g of Microdol H200, 101.3g of China Clay Supreme and 131.4g of Tioxide TR92 were weighed into a separate container and then added to the

1 litre container. A further 131.4g of Tioxide TR92 was added to the disperser container. The disperser speed was gradually increased to 2000rpm and maintained at this speed for a further 5 to 10 minutes during which the pigment and extender started to disperse. A further 70.8g of water was added followed by 1.5g of Natrosol Plus Grade, the latter added carefully to the top of the vortex formed in the millbase through stirring. As dispersion proceeded the viscosity of the millbase rose and the speed of the disperser was raised to approximately 3000rpm in order to maintain good circulation of the millbase as evidenced by a vortex extending to about halfway into the mixture following the addition of the Natrosol Plus Grade the millbase was dispersed for a total of 25 minutes after which 0.2g of Rocima V189 was added.

Paint make-up

To 729.0g of the millbase was added 3.8g of water and stirred at about 600rpm using a paddle stirrer. Whilst stirring the diluted millbase 220.9g of the aqueous dispersion of modified acrylic binder polymer made according to Example 6 was also added followed by 0.4g of ammonia solution finally the stirrer speed was raised to 900rpm and the thickeners were added, comprising 11.5g of Acrysol SCT-275 and 4.8g of Aquaflow NHS300. The

resulting paint was stirred for approximately 5 to 10 minutes following the thickener addition and allowed to stand for 16 hours at room temperature. The PVC (total) was 58.2% and the PVC (TiO_2) was 25.8%. The contrast ratio was measured at 98.1%.

Comparative Example E

A millbase was made according to Example 7 except that 28.3g of the initial charge of water were replaced by a solvent mixture consisting of 8.1g of benzyl alcohol and 20.2 of Texanol.

To 729.0g of millbase was added 10.9g of water and stirred at about 600rpm using a paddle stirrer. 192.7g of the aqueous dispersion made according to Comparative Example D was added whilst stirring. The remaining additions and conditions were identical to those of Example 7.

The PVC (total) was 58.2% and the PVC (TiO_2) was 25.8%. The contrast ratio was 94.1%.

Example 8

A paint was made using the ingredients and according to the method of Example 7 except that the amount of Tioxide TR92 pigment was reduced to achieve a PVC (total) of 55.2% and a PVC (TiO_2) of 20.9%. The contrast

ratio was measured to be 94.6%. This is comparable to the contrast ratio of Comparative Example E that used a significantly higher PVC (TiO₂) of 25.8%

CLAIMS

1. A film-forming binder polymer for a coating composition wherein the polymer is modified by the presence of bonded moieties obtainable from plant fibre gum.
2. A film-forming binder polymer as claimed in Claim 1 wherein the plant fibre gum is obtainable from corn fibre gum.
3. A binder polymer as claimed in Claim 1 or Claim 2 wherein the polymer is modified by bonded moieties derived from furanose.
4. A binder polymer as claimed in Claim 1 wherein the bonded moieties are derived by adding plant fibre gum to the polymerisation reaction mixture from which the binder polymer is formed.
5. A binder polymer as claimed in Claim 4 wherein the plant fibre gum is corn fibre gum.
6. A binder polymer as claimed in Claim 3 wherein the binder moieties derived from furanose are derived by having furanose present in the polymerisation reaction mixture from which the binder polymer is formed.
7. A binder polymer according to any one of the preceding claims wherein the polymer is an aqueous dispersion of particles.
8. A process for modifying film-forming binder polymers which are binder polymers for coating compositions wherein plant fibre gum is

added to the polymerisation reaction which produces the binder polymer.

9. A process as claimed in Claim 8 wherein the plant binder gum is corn fibre gum.

5 10. A process for modifying film-forming binder polymers which are binder polymers for coating compositions wherein furanose is added to the polymerisation reaction which produces the binder polymer.

11. A coating composition wherein the composition contains a modified binder polymer as claimed in any one of the preceding claims.

10 12. A coating composition according to Claim 11 wherein the composition further contains at least one component selected from the group consisting of pigments, fillers, extenders, rheological modifiers, dispersants, antifoams, flow aids, crosslinkers and biocides.

15 13. A coating composition according to claim 12 wherein the selected component is pigment.

14. A coating composition according to Claim 13 wherein the pigment is titanium dioxide.

20 15. A coating composition according to Claim 14 wherein the pigment is rutile.

16. A coating composition according to any one of Claims 13 to 15 having a PVC(TiO_2) of from 10 to 35%.
17. A method for improving the opacity of coating compositions wherein the method comprises employing a modified binder polymer according to any one of Claims 1 to 7 as a binder in a coating composition.
18. A method for improving the opacity of coating compositions comprising particulate non-film forming materials wherein the method comprises employing a modified binder polymer according to any one of Claims 1 to 7 as a binder.
19. A method for improving the opacity of coating compositions according to Claim 18 wherein the particulate non-film forming material is titanium dioxide.
20. A method for improving the opacity of coating compositions according to Claim 18 wherein the particulate non-film forming material is rutile.

ABSTRACT

A film-forming binder polymer for a coating composition such as a
5 paint, varnish or woodstain where the polymer is modified by the presence
of bonded moieties derived from plant fibre gum, especially corn fibre gum
and more particularly moieties derived from furanose. The modified binder
polymer minimises the need to use coalescing solvents without creating
excessive tackiness and improves the scrub resistance of dried coats of paint
10 and also improves the opacity of the dried coating composition.

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